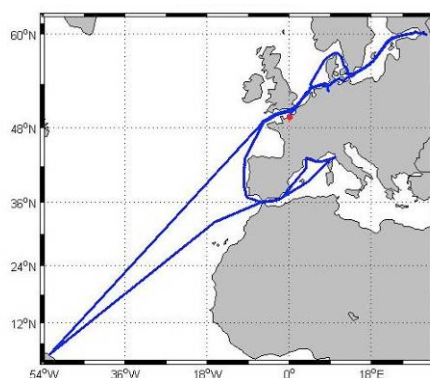


AX20 Readme File

Platform Information

In February 2006, IRD installed an instrument to measure CO₂ in surface water on the MN Colibri. The vessel cruises from Europe to French Guyana (Kourou). 5 to 7 voyages are expected every year.



The CO₂ analyser was designed and built by Craig Neil. It is fully automated. On MN Colibri, it is located in the ship's bow thruster space. A Seabird SBE21 thermosalinograph is installed on the same sea water inlet piping. An air inlet is placed on top of the bridge. It allows atmospheric CO₂ measurements in conjunction with surface water CO₂ observations.

Cruise information

Survey type: VOS line
Vessel Name: MN Colibri
Country vessel: FR
Call sign: FNHO

Period: 14-24 May 2010

Geographical coverage: Atlantic Ocean

Bounds:

Westernmost longitude: 52°W
Easternmost longitude: 7°W
Northernmost latitude: 48°N
Southernmost latitude: 8°N

Class of Data: Surface ocean carbon dioxide concentrations

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CO₂ sensors (xCO₂)

The accuracies of all components, when operating optimally, are such that the calculated seawater fCO₂ has an accuracy of 2 µatm or better and the calculated mole fraction of CO₂ in air (xCO₂) has an accuracy of 0.1 µatm.

Infrared Analyzer

LI-COR model 6262 (February 2006 - present)

ftp://ftp.licor.com/perm/env/LI-6262/Manual/LI-6262_Manual.pdf

CO₂ resolution: 0.01 µmol/mol

CO₂ accuracy: ± 1 ppm at 350 ppm

Pressure resolution: 0.02 hPa

Internal pressure transducer accuracy: ± 1.2 hPa

(Manufacturer specifications: ±0.1% FS, where FS = 0-1150 hPa)

The general principle of instrumental design can be found in Pierrot et al. (2009). The concentration of CO₂ in the headspace gas was measured using the adsorption of infrared (IR) radiation by the CO₂ molecule. The LI-COR analyzer passed IR radiation through two cells. The reference cell is constantly flushed with a reference gas CO₂-free. The sample cell is flushed with the gas of interest (standard, outside atmosphere, or headspace gas from equilibration chamber).

The infrared analyzer is calibrated regularly using three standard gases (~250~500 ppm) from Air Liquide - France, which were calibrated at DT INSU against primary NOAA standards.

The exact concentrations of the standards are:

0 ppm (nitrogen gas)

246.3 ppm

366.9 ppm

506.1 ppm

CO₂ in marine air method (xCO₂)

Outside air was constantly being pulled (~6 liters/min) from an inlet on the top of the bridge through ~30 m of tubing (1/4" OD Dekabon) to the analytical system. The flushing rate of the LI-COR analyzer during ATM analyses is ~70-150 ml/min.

Drying: The effects of water vapor on the sample analyses were kept to a minimum by removing as much water as possible. The water was first condensed out of the sample gas stream by cooling to ~5° C using a thermoelectric device. Then water was further removed using Nafion® gas dryers before reaching the IR analyzer. The counterflow gas in the dryer is pre-dried outside air. Typical water content of the analyzed gas was less than 3 millimoles/mole with approximately 90% of the water being removed.

Sampling and equilibrator design

The seawater inlet is on the sea chest at an approximate depth of 3 meters. Seawater was pushed through a spray head into an equilibration chamber that was fabricated using a filter housing (ColeParmer, U-010509-00). The chamber had a ~0.5 L water reservoir and a ~0.8 L

gaseous headspace. Water flow rate was ~2 - 3 L/min. The rate at which the headspace gas recirculated through the analyzer during EQU analyses was ~70 - 150 ml/min.

The equilibration chamber was vented to the surrounding space.

Drying: The effects of water vapor on the sample analyses were kept to a minimum by removing as much water as possible. The water was first condensed out of the sample gas stream by cooling to ~5° C using a thermoelectric device. Then water was further removed using Nafion® gas dryers before reaching the IR analyzer. The counterflow gas in the dryer is pre-dried outside air. Typical water content of the analyzed gas was less than 3 millimoles/mole with approximately 90% of the water being removed.

A typical sequence of the continuous analyses was:

| STEP | TYPE | REPETITIONS |
|------|-----------------|-------------|
| 1 | Standards (all) | 1 |
| 2 | ATM | 6 |
| 3 | EQU | 90 |

Sea Surface Temperature (SST) and Salinity (SSS)

SeaBird model SBE-21 (February 2006 - Present)

http://www.seabird.com/pdf_documents/manuals/21_026.pdf

Temperature resolution: 0.001°C

Temperature accuracy: ± 0.01°C

Salinity resolution: 0.002 ‰

Seawater samples are taken daily at the thermosalinograph outlet. Samples are analysed at SHOM-France in an OSIL Portasal, and compared to IAPSO Sea Water Standards.

The salinity accuracy is expected to be ± 0.02 ‰

The thermosalinograph is calibrated every 18 months, either at Seabird-USA or at SHOM-France.

The seawater inlet of both CO₂ analyser and TSG is located on the sea chest. The TSG is very close to the hull, the sea water flow rate is 30 l/min. We consider that the temperature inside the TSG is the SST. The warming between the TSG and the CO₂ analyser is 0.2°C (T_{equ} – T_{TSG}).

Equilibrator Temperature (T_{equ})

During the first configuration (February 2006 – April 2007), the water temperature in the equilibrator was measured with an Omega RTD PR-11-2-100-1 temperature probe, whose tip was submerged about 5 cm.

During the second configuration (April 2007 – Present), the water temperature was measured with a Hart 1521 thermometer. This thermometer was calibrated at SHOM - France in October 2009.

Superlogics RTD module 8013 (February 2006 – April 2007) with an Omega RTD PR-11-2-100-1 temperature probe.

http://www.superlogics.com/sl_details.asp?prod=782

Accuracy: ± 0.05%.

Hart model 1521 (April 2007 - present) with a 5610 thermistor probe

http://www.testequipmentdepot.com/hart/pdfs/1521_1522.pdf

Resolution: 0.001°C

Accuracy: $\pm 0.025^{\circ}\text{C}$

This thermometer was calibrated at SHOM - France in October 2009.

Atmospheric Pressure (Patm)

Druck barometer RPT350 (February 2006 - present)

<http://www.ge-mcs.com/en/pressure-and-level/transducerstransmitters/rtp350.html>

Accuracy: $\pm 0.01\%$

The barometric pressure was measured in the bridge, ~20 m above the equilibrator. The Druck barometer is placed in a box, which also contains the GPS and the Iridium transmitter.

Equilibrator Pressure (Pegu)

The pressure in the equilibrator relative to the bow thruster compartment was measured with a Setra model 239 differential barometer. The LI-COR barometer measured the barometric pressure of the compartment.

Setra model 239, differential pressure (February 2006 - present)

http://www.setra.com/ProductDetails/model_239.htm

Resolution: 0.01 hPa

Accuracy: ± 0.052 hPa

(manufacturer specifications: $\pm 0.14\%$ FS, where FS = ± 7.5 inches WC)

The absolute pressure of the equilibrator headspace reported in data files is the sum of the infrared analyzer pressure and the differential pressure from the pressure transducer attached to the equilibrator.

Variables info

| Column header | Explanation |
|---------------|---|
| dd | Day |
| mm | Month |
| yy | Year UTC date |
| hh | Hours UTC time |
| mn | Minutes |
| ss | Seconds |
| day | Decimal year day |
| Lon | Longitude in decimal degrees (negative values in west) |
| Lat | Latitude in decimal degrees (negative values in southern hemisphere) |
| sst | Temperature from the ship's thermosalinograph ($^{\circ}\text{C}$) |
| sss | Salinity from the ship's thermosalinograph (psu) |
| Patm | Atmospheric pressure in millibar |
| Tequ | Equilibrator temperature ($^{\circ}\text{C}$) |
| xCO2 | Mole fraction of CO ₂ (dry) in air or equilibrated air (ppm) |
| H2Omm | Water content of Licor in mmol/mol |
| Pegu | Pressure in equilibrator (mbar) |
| fCO2sw | Fugacity in CO ₂ in seawater (μatm) |

CALCULATIONS:

Mixing ratios of dried equilibrated headspace and air, corrected from the Licor drift ($x\text{CO}_2$), are converted to fugacity of CO_2 in surface seawater and water saturated air in order to determine the $f\text{CO}_2$.

For ambient air and equilibrator headspace the $f\text{CO}_{2a}$, or $f\text{CO}_{2eq}$ is calculated assuming 100% water vapor content:

$$f\text{CO}_{2eq} = x\text{CO}_{2eq} (P - p\text{H}_2\text{O}) \exp(B11 + 2 \delta 12) P/RT$$

where $f\text{CO}_{2eq}$ is the fugacity in the equilibrator, $p\text{H}_2\text{O}$ is the water vapor pressure at the sea surface temperature, P is the atmospheric pressure (in atm), T is the SST or equilibrator temperature (in K) and R is the ideal gas constant ($82.057 \text{ cm}^3 \cdot \text{atm} \cdot \text{deg}^{-1} \cdot \text{mol}^{-1}$). The exponential term is the fugacity correction where $B11$ is the second virial coefficient of pure CO_2

$$B11 = -1636.75 + 12.0408 T - 0.032795 T^2 + 3.16528 \times 10^{-5} T^3$$

and

$$\delta 12 = 57.7 - 0.118 T$$

is the correction for an air- CO_2 mixture in units of $\text{cm}^3 \cdot \text{mol}^{-1}$ (Weiss, 1974).

The calculation for the fugacity at SST involves a temperature correction term for the change of $f\text{CO}_2$ due to changes in water temperature which when the water passes through the pump and through the rubber tubing within the ship. The water in the equilibrator is typically 0.2°C warmer than sea surface temperature.

The empirical temperature correction from equilibrator temperature to SST was:

$$f\text{CO}_2(\text{SST}) = f\text{CO}_2(\text{eq}) \exp (-0.0423 (T_{eq} - \text{SST}))$$

where SST is the sea surface temperature and T_{eq} is the equilibrator temperature in $^\circ\text{C}$.

METHOD REFERENCES:

- Pierrot, D., C. Neill, K. Sullivan, R. Castle, R. Wanninkhof, H. Luger, T. Johannessen, A. Olsen, R. A. Feely, and C. E. Cosca (2009). Recommendations for autonomous underway $p\text{CO}_2$ measuring systems and data-reduction routines. *Deep Sea Research II*, 56: 512-522.
- Weiss, R. F. (1974). Carbon dioxide in water and seawater: the solubility of a non-ideal gas. *Mar. Chem.* 2: 203-215.